Elastic constants of nematic liquid crystals of uniaxial symmetry

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Abstract

We study in detail the influence of molecular interactions on the Frank elastic constants of uniaxial nematic liquid crystals composed of molecules of cylindrical symmetry. A brief summary of the status of theoretical development for the elastic constants of nematics is presented. Considering a pair potential having both repulsive and attractive parts numerical calculations are reported for three systems MBBA, PAA and 8OCB. For these systems the length-to-width ratio x_0 is estimated from the experimentally proposed structure of the molecules. The repulsive interaction is represented by a repulsion between hard ellipsoids of revolution (HER) and the attractive potential is represented by the quadrupole and dispersion interactions. From the numerical results we observe that in the density range of nematics the contribution of the quadrupole and dispersion interactions are small as compared to the repulsive HER interaction. The inclusion of attractive interaction reduces the values of elastic constants ratios. The temperature variation of elastic constants ratios are reported and compared with the experimental values. A reasonably good agreement between theory and experiment is observed.

1   Introduction

In a previous paper [1] (here after reffered to as I), we developed a theory based on the density functional formalism [2] for the deformation free-energy of any systems with continuous broken symmetry, and applied the theory to derive expressions for the elastic constants of nematic and smectic-A phases of uniaxial ($D_{\infty h}$) symmetry. These expressions of elastic constants are written in terms of order parameters that characterize the nature and amount of ordering in the phase and the structural parameters involving the generalized spherical harmonic coefficients of the direct pair correlation function of an effective isotropic liquid, the density of which is determined using a criterion of the weighted density functional formalism [3].

In the present paper we restrict ourselves to the uniaxial nematic phase. According to the continuum theory [4], the bulk elastic properties of nematics can be described by three elastic constants, associated with the restoring forces opposing splay (K_1), twist (K_2) and bend (K_3) distortions. The distortion free energy density is written as

$$\frac{1}{V}\Delta A_e = \frac{1}{2}[K_1(\nabla \cdot \hat{\mathbf{n}})^2 + K_2(\hat{\mathbf{n}} \cdot \nabla \times \hat{\mathbf{n}})^2 + K_3(\hat{\mathbf{n}} \times \nabla \times \hat{\mathbf{n}})^2] \qquad (1)$$

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where $\hat{\mathbf{n}}$, the director, indicates the preferred direction of the long-axes of the molecules. These elastic constants play an important role in characterizing liquid crystal displays. It is difficult to measure experimentally the absolute values of these elastic constants [5, 6, 7, 8]. Their ratios K_2/K_1 and K_3/K_1 can be measured more accurately [8, 9, 10]. For high duty liquid crystal displays [11], the ratio K_3/K_1 is desired to be as small as possible. The elastic moduli are temperature and density dependent. The dependence on the density is pronounced. A number of measurements are reported which show that K_1 and K_2 have weak temperature dependences whereas K_3 rapidly increases with temperature and that when the nematic-smectic A transition temperature is approached from above, K_1 does not show any sharp change but K_2 and K_3 increases anomalously.

The present paper is organized as follows: In sec.2, we describe, in brief, the status of the theoretical development for the elastic constants of the nematics and summarize the working equations used in the calculation. The numerical evaluation and results are presented in sec.3

2 Theoretical development and working equations

First we shall comment, in brief, on the status of the theoretical development for the elastic constants of nematics. A detail of these works are well documented elsewhere [10, 12]

In the Landau-de-Gennes theory the free-energy density is assumed to be an analytic function of the order parameter tensor. To the extent that the order parameter is small, the free-energy density is expressed as an expansion in its various orders and gradient terms. The elastic free-energy density upto second order in order parameter is written in terms of two elastic constants L_1 and L_2 which are related with the Frank elastic constants as

$$K_1 = \frac{q}{2}(L_1 + \frac{1}{2}L_2)\overline{P_2}^2 \tag{2}$$

$$K_2 = \frac{q}{2}L_1\overline{P_2}^2 \tag{3}$$

and

$$K_1 = K_3 \tag{4}$$

Thus the elastic constants moduli K_i vary with temperature like $\overline{P_2}^2$. The prediction $K_1{=}K_3$ is not consistent with the experimental observation. However, this is an artifact of the derivation in which only the gradient terms of $\overline{P_2}$ order parameter have been considered. If $\overline{P_4}$ term is also included in the free-energy expansion, all the three elastic constants will be different. Using an expansion of the intermolecular potential

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in spherical harmonics Priest [14] also arrived at the same conclusion. For the special case of dispersion forces, Nehring and Saupe [13] calculated (up to the second order $\overline{P_2}$) the ratio of the elastic constants

$$K_1 : K_2 : K_3 = 5 : 11 : 5$$

Apart from the temperature dependence of the elastic constants, via $\overline{P_2}$ order parameter, there is also a dependence on the density. Priest [14] showed that the deviation from the equality $K_1 = K_3$ are related in a simple way to the ratio $\overline{P_4}/\overline{P_2}$ and

$$K_1/\overline{K} = \Delta - \Delta'(\overline{P_4}/\overline{P_2}) + \dots \tag{5}$$

$$K_2/\overline{K} = -2\Delta - \Delta'(\overline{P_4}/\overline{P_2}) + \dots \tag{6}$$

$$K_3/\overline{K} = \Delta + 4\Delta'(\overline{P_4}/\overline{P_2}) + \dots \tag{7}$$

where $\overline{K} = \frac{1}{3}(K_1 + K_2 + K_3)$. For the case of hard spherocylinders, the constants Δ and Δ' were found to depend on the length-width ratio of the molecules. Most of the hard rod models [10] are strictly valid only for the very long and thin rods and they usually predict too large a value for K_3 and cannot reproduce the temperature dependences of the elastic constants.

Several workers [10] have evaluated the elastic constants for the van der Walls type potential described by hard spherocylinders with superimposed attractive interactions.While Stecki and Poniewierski [15] treatment is based on the the direct correlation function approach, mean field (MF) approximation has been adopted by Kimura et. al. [16]. These authors found that $K_3 > K_1 > K_2$ and that the temperature dependence of their ratios is in accordance with the experiment. Using generalized van der Walls (GVDW) theory [17], which couples the contributions of the short-and long-range pair potentials, the elastic moduli were evaluated in a model based on the distributed harmonic forces [18] between the molecules. In this work both the repulsive and attractive forces have been considered as distributed along the molecules. This approach disregards the temperature dependence of elastic constants and assumes perfect orientational order i.e. $\overline{P_2} = \overline{P_4} = 1$. It is a variant on the ideas of Gelbart and co-workers [17] who studied the combined effect of repulsive and attractive forces. Zakhrov [19] evaluated the elastic constants and order parameters by using a theory that is based on the method of conditional distribution (MCD) [20]. This method introduces a concept of reduced distribution functions which obey infinite chains of integro-differential equations. For an arbitrary equations of the chains based on the concept of the mean-force potential (MFP) [21, 22] a truncated procedure was adopted. The numerical solution exhibits certain qualitative features: The order parameters decrease with increasing volume and temperature. While the observed value of $K_1/\overline{K}$ and $K_2/\overline{K}$ increases with increasing volume, the values of

$K_3/\overline{K}$ decreases with it. $K_1/\overline{K}$ increases strongly with the length-width ratio and $K_2/\overline{K}$ decreases with it, and $0.5 < K_3/K_1 < 3.0$ and $0.5 < K_2/K_1 < 0.8$

Several workers have considered the application of density functional theory to study the elastic properties of nematics. A detail account of these works are summarized elsewhere by one of us [10]. In this theory exact expression for the elastic free- energy is obtained in terms of order parameters and direct correlation functions. The correlation of the ordered phases are, in general, not known and hence to be approximated. The functional Taylor expansion is performed to obtain the n-particle direct correlation function of an inhomogeneous system from the n- and higher-order direct correlation functions of an uniform system. The elastic constants of nematics were calculated for a number of model systems using approximate forms of the pair correlation function of the medium. However, none of these approximate forms of the pair correlation function gives the structure of the medium correctly, and so the result reported are not expected to be accurate.

A unified molecular theory was developed by Singh et. al. [1] for the deformation free-energy of ordered molecular phases. This theory is based on the weighted density functional formalism [3] and writes the exact expressions for the elastic constants, in terms of integrals involving spherical harmonic coefficients of the direct pair correlation function of an effective isotropic liquid . Adopting the procedure as outlined in I, we express the elastic free- energy density for a uniaxial nematic phase of axially symmetric molecules.

$$
\begin{aligned}
\frac{1}{V}\beta\Delta A_e[\rho] &= -\frac{1}{2}\rho_n{}^2\sideset{}{'}\sum_{l_1 l_2 l}\sum_{m}[\frac{(2l_1+1)(2l_2+1)}{(4\pi)^2}]^{\frac{1}{2}}\overline{P}_{l_1}\overline{P}_{l_2}C_g(l_1 l_2 l, omn) \\
&\quad \int d\mathbf{r_{12}}C_{l_1 l_2 l}(\mathbf{r_{12}})[(\frac{4\pi}{2l_2+1})^{\frac{1}{2}}Y_{l_2 m}(\Delta\chi(\mathbf{r_{12}})) - 1]Y_{lm}^*(\hat{\mathbf{r}}_{12})
\end{aligned}
\qquad (8)
$$

where ρ_n is the nematic number density and $\overline{P}_l$ are the Legendre polynomial order parameters. The prime on the summation indicates that l_1 and l_2 are even $\hat{\mathbf{r}}_{12} = \mathbf{r}_{12}/|\mathbf{r}_{12}|$ is unit vector along the intermolecular axis, C_g are the Clebsch-Gordan coefficients, $C_{l_1 l_2 l}$ are the spherical harmonic coefficients of the direct pair correlation function of an isotropic liquid, and $\Delta\chi(\mathbf{r}_{12})$ represents the angle between the principal director at $\mathbf{r_1}$ and $\mathbf{r_2}$. Confining the variation of director at $\mathbf{r_2}$ in a plane, the $Y_{l_2 m}(\Delta\chi(\mathbf{r}_{12}))$ is expressed in terms of the distortion angle which is assumed to be small. Performing the angular integration over $\hat{\mathbf{r}}_{12}$ and comparing eq. (8) with eq. (1), the following expressions for the elastic constants of uniaxial nematic phase composed of cylindrically symmetric molecules are obtained [1],

$$
\beta K_i = \sideset{}{'}\sum_{l_1, l_2}\beta K_i(l_1, l_2)
\qquad (9)
$$

The explicit expressions for the first few terms of the series can be written as

$$\beta K_1(2,2) = (\frac{5}{4\pi})^{\frac{1}{2}}\rho_n^2\overline{P}_2^2[\frac{1}{2}J_{220} - \frac{1}{\sqrt{14}}J_{222}] \tag{10}$$

$$\beta K_1(2,4) = -\frac{3}{4}(\frac{5}{\sqrt{14\pi}})\rho_n^2\overline{P}_2\overline{P}_4 J_{242} \tag{11}$$

$$\beta K_1(4,4) = (\frac{5}{4\pi})^{\frac{1}{2}}\rho_n^2\overline{P}_4^2[\sqrt{5}J_{440} - \frac{13}{2\sqrt{77}}J_{442}] \tag{12}$$

$$\beta K_2(2,2) = (\frac{5}{4\pi})^{\frac{1}{2}}\rho_n^2\overline{P}_2^2[\frac{1}{2}J_{220} + \sqrt{\frac{2}{7}}J_{222}] \tag{13}$$

$$\beta K_2(2,4) = \beta K_1(2,4) \tag{14}$$

$$\beta K_2(4,4) = (\frac{5}{4\pi})^{\frac{1}{2}}\rho_n^2\overline{P}_4^2[\sqrt{5}J_{440} + \frac{47}{2\sqrt{77}}J_{442}] \tag{15}$$

$$\beta K_3(2,2) = \beta K_1(2,2) \tag{16}$$

$$\beta K_3(2,4) = -\frac{4}{3}\beta K_1(2,4) \tag{17}$$

and

$$\beta K_3(4,4) = (\frac{5}{4\pi})^{\frac{1}{2}}\rho_n^2\overline{P}_4^2[\sqrt{5}J_{440} + \frac{17}{\sqrt{77}}J_{442}] \tag{18}$$

In this expressions the structural parameter $J_{l_1 l_2 l}$ are defined as

$$J_{l_1 l_2 l} = \int r_{12}^4 dr_{12} C_{l_1 l_2 l}(r_{12}) \tag{19}$$

3   Calculation and Results

As obvious from eq. (9) the evaluation of elastic constants requires the values of density, order parameters $\overline{P}_2$ and $\overline{P}_4$ (as a function of temperature), the structural parameters $J_{l_1 l_2 l}$ (as a function of density and length-width ratio x_0) and potential parameters. In I it was shown that the dipole-dipole and dipole-quadrupole interactions do not contribute to the free energy (and hence elastic constants) of the uniaxial mesophases. For the numerical calculation we consider a system of molecules with prolate ellipsoidal symmetry interacting via a pair potential,

$$u(\mathbf{r_{12}}, \Omega_1, \Omega_2) = (u_{HER} + u_{qq} + u_{dis})(\mathbf{r_{12}}, \Omega_1, \Omega_2) \tag{20}$$

where u_{HER} represents the repulsion between hard ellipsoids of revolution (HER) and the subscripts qq and dis indicate respectively, the interactions arising due to the

quadrupole-quadrupole and dispersion forces. The explicit from of these interactions are given in I.

For evaluating structural parameters , $J_{l_1 l_2 l}$, as a function of density and x_0, the values of spherical harmonic coefficients $C_{l_1 l_2 l}$ for the potential model (20) are needed. The $C_{l_1 l_2 l}$ can be obtained by solving the Ornstein- Zernike (OZ) equation, using the Percus-Yevick (PY) closure relations. As this evaluation is difficult, in a calculation only a finite number of spherical harmonic coefficients for any orientation dependent function can be handled. It has been shown that for the potential model (20) the inclusion of all the harmonics up to indices l_1, $l_2 = 4$ makes the series fully convergent.

In this paper we study in detail the influence of HER, qq, dispersion interactions on the elastic properties of three uniaxial nematic liquid crystals: p-azoxyanisole (PAA), N-p-methoxybenzylidene-p-butylaniline (MBBA) and 4'-pn-octyloxy-4-cyanobiphenyl ($8OCB$). For these systems we have estimated the values of length-width ratio x_0 from the proposed structure of molecules as determined by ^{14}N nuclear quadrupole resonance [23] and line shape [24] studies. The estimated values of x_0 are 2.68, 2.87 and 4.88 for MBBA , PAA and 8OCB, respectively. The PY closure relation have been solved by Ram and Singh [25] for the g_{HER}, h_{HER} and C_{HER} harmonics for $x_0 = 3.00$, 3.25, 3.50 and 4.00. Taking their results we estimated in I C-harmonics for the quadrupolor and dispersion interactions. Adopting similar procedure we have evaluated here these harmonics for $x_0 = 2.68$, 2.87, and 4.88. With known C- harmonics we evaluated the values of structural parameters as a function of reduced density $\rho^*(\ = \rho_n d_0^3)$ where d_0 is the molecular diameter. In addition to $J_{l_1 l_2 l}$ we need the values of order parameters $\overline{P_2}$ and $\overline{P_4}$ as a function of temperature and of potential parameters ϵ_0 / k, d_0 and quadrupole moment Θ. Here ϵ_0 is constants with unit of energy. In the calculation we use the values of $\overline{P_2}$ as determined by the experiments and estimate $\overline{P_4}$ as $\overline{P_4} / \overline{P_2} \cong \overline{P_2}^2$

We calculate the contribution of the individual terms of the series

$$K_i = K_i(2,2) + 2K_i(2,4) + K_i(4,4) \tag{21}$$

for the HER, qq and dispersion interactions for three values of $x_0(= 2.68(\text{MBBA})$, 2.87(PAA) and 4.88 (8OCB)). A number of observations regarding relative contributions of these interactions terms have been made from this calculation: In the density range of nematics the contribution of quadrupole and dispersion interactions are small as compared to the repulsive HER interaction. The absolute values of elastic constants are sensitive to the values of molecular parameters. The inclusion of dispersion and quadrupole interactions reduce the values of elastic constants ratios. For a given x_0, $K_3^{HER}(2,4)$ is positive where as $K_2^{HER}(2,4)$ and $K_1^{HER}(2,4)$ are negative. Consequently we find that $K_3^{HER} > K_1^{HER} > K_2^{HER}$ and the ratio $(K_3^{HER}/K_1^{HER}) > (K_2^{HER}/K_1^{HER})$. This result is in accordance with the simulation

work [27]. The absolute values of K_i^{HER} increase linearly with the temperature and the values of their ratios do not change with temperature. In case of the quadrupole interaction for a given x_0 and quadrupole moment Θ the contribution of $K_i^{qq}(4,4)$is much smaller as compared to $K_i^{qq}(2,2)$. As the values of Θ increases the contribution of each individual terms of the series (21) and K_i^{qq} increase significantly. The numerical values of K_1^{qq} and K_3^{qq} are positive where as K_2^{qq} is negative. The influence of the dispersion interaction is small as compared to the quadrupole interaction

The temperature dependence of the elastic constants are mainly due to the variation of $\overline{P_2}$ and $\overline{P_4}$ with temperature. We calculate the values of K_i using the experimental values of $\overline{P_2}$. Using available experimental data of $\overline{P_2}$ for PAA [27] and MBBA [28] we draw a smooth curve and the values of $\overline{P_2}$ used in the calculation correspond to this smooth curve. For 8OCB we use the experimental values of $\overline{P_2}$ as measured by Madhusudana and Pratibha [9]. We have found that the values of $\overline{P_4}$ for PAA as estimated from the relation $\overline{P_4} \cong \overline{P_2}^3$ are in good agreement with experimental data [29] of deuteriated PAA obtained from the coherent neutron scattering experiment. So in the calculation we use this estimated values of $\overline{P_4}$

Experimentally it is difficult to obtain the absolute values of elastic constants. It is the ratios K_2/K_1 and K_3/K_1 which are usually measured more accurately. In addition to these ratios the other quantity which one finds accurately from the experiment is $K_i/\overline{K}$. In accordance with the experiment we observe that the ratio K_3/K_1 decreases significantly with increasing temperature whereas the ratio K_2/K_1 is more or less independent of the temperature. So in the following figures we show a comparison between the theoretical and experimental values of the ratios K_3/K_1, $K_1/\overline{K}$ and $K_3/\overline{K}$ for the PAA, MBBA and 8OCB.

A comparison between the experimental [30, 31] and theoretical values of ratios K_3/K_1, $K_1/\overline{K}$ and $K_3/\overline{K}$ for PAA is shown in fig.1. It can be seen that the theoretical values are consistent with the experimental data. We have found that the inclusion of quadrupole and dispersion interactions decreases the values of elastic constants ratios. Figure 1 shows that the ratio K_3/K_1 decreases significantly with temperature. A weak temperature dependence is found for the ratios $K_i/\overline{K}$. As temperature increases the value of $K_3/\overline{K}$ decrease whereas $K_1/\overline{K}$ increases. As obvious from fig. 2 a similar trend in the variation of these ratios has been found for MBBA. In case of 8OCB fig.3 a similar but more pronounced variation of these ratios with temperature is observed. Further, as physically expected near the nematic-smectic A transition a pronounced increase in the value of K_3 is clearly observed.

Table 1 shows the variation of elastic constants ratios with length-width ratio near nematic-isotropic transition temperature. It can be seen that with x_0 the ratio K_3/K_1 and $K_3/\overline{K}$ increase whereas $K_1/\overline{K}$ and $K_2/\overline{K}$ decrease.

As mentioned in the text, the values of elastic constants are sensitive to the

Table 1: Ratio of elastic constants of nematic liquid crystals near nematic-isotropic transition temperature T_{NI}

x_0	$\frac{K_3}{K_1}$	$\frac{K_3}{\overline{K}}$	$\frac{K_1}{\overline{K}}$	$\frac{K_2}{\overline{K}}$
2.68	1.211	1.276	1.053	o.747
2.87	1.458	1.34	0.919	0.739
4.88	1.542	1.409	0.917	0.682

values of the structural parameters, order parameters and potential parameters. The available information about these parameters are not acurate. So as our knowledge of these parameters improves, more accurate values of elastis constants will result.
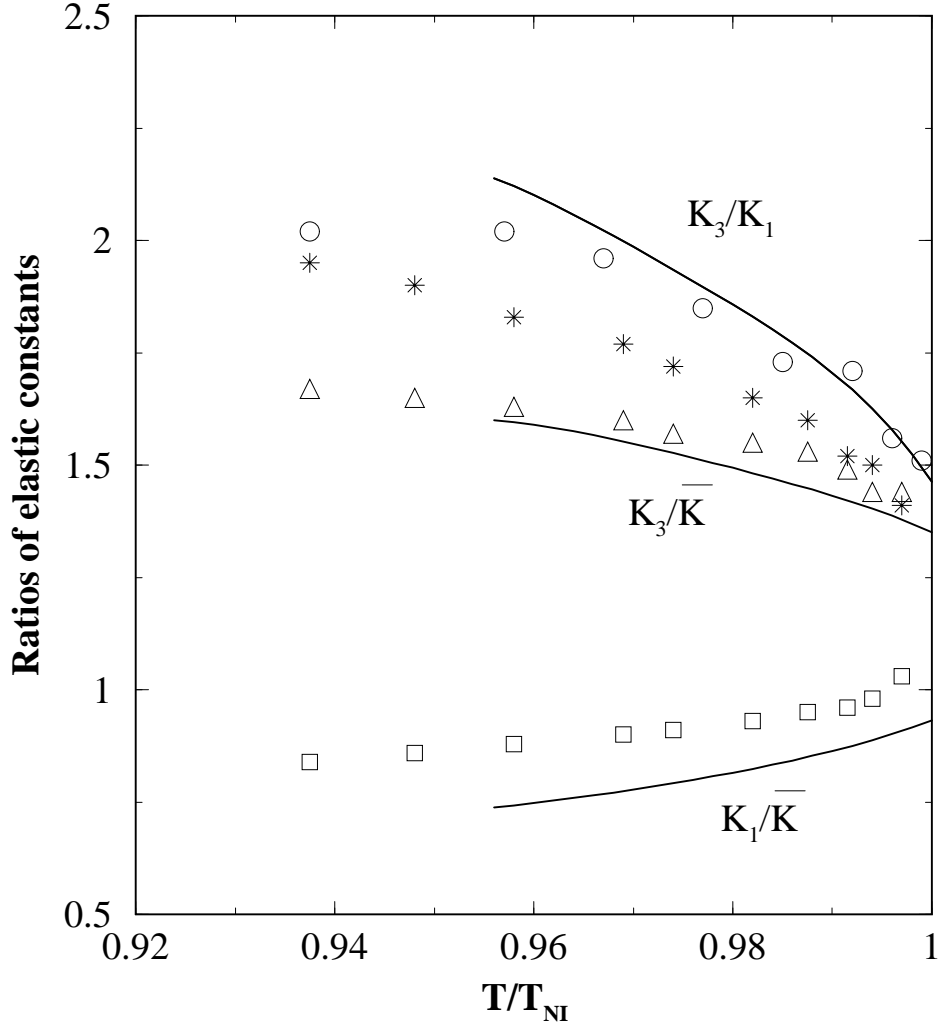
Figure 1: Comparison between the calculated (solid lines) and experimental values of the elastic constants ratios for PAA as a function of temperature. The experimental ratios o[30], *[31] are shown as K_3/K_1 ; o and * ; $K_3/\overline{K}$; Δ and $K_3/\overline{K}$; square
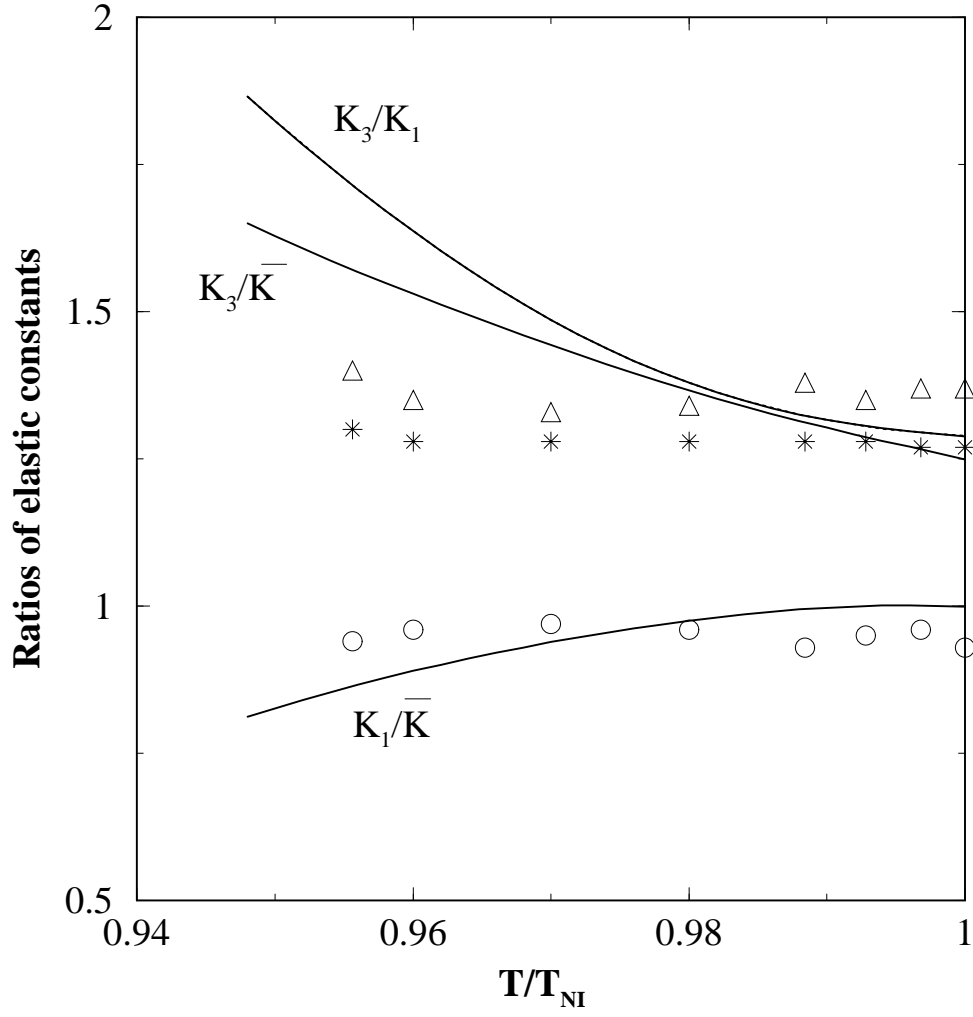
Figure 2: Comparison between the calculated (solid lines) and experimental values [32] of the elastic constants ratios for MBBA as a function of temperature. The experimental ratios are shown as K_3/K_1 : $\triangle$; $K_3/\overline{K}$: * and $K_1/\overline{K}$: o
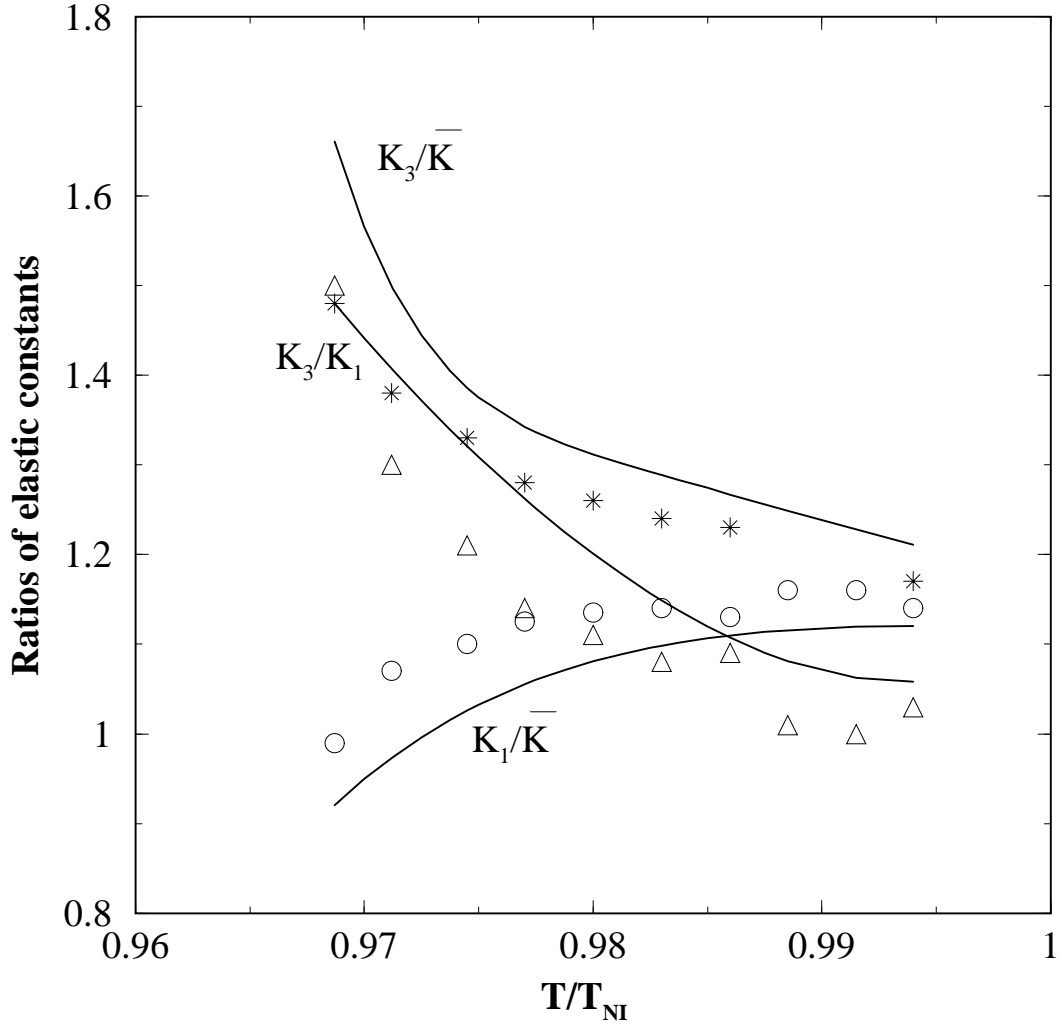
Figure 3: Comparison between the calculated (Solid lines) and experimental[9] values of elastic constants ratios for 8OCB as a function of temperature. The experimental ratios are shown as $K_3/K_1 : \triangle$; $K_3/\overline{K}$: * and $K_1/\overline{K}$: o

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